

## Ethylene on graphite: Heats of adsorption and phase diagram

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Isosteric heats of adsorption ( $q_{st}$ ) of ethylene on Grafoil MAT have been measured calorimetrically in the region  $98 < T < 120$  K over a broad range of surface coverages up to the equivalent of 3.7 adsorbed layers. For coverages less than the equivalent of a  $\sqrt{3} \times \sqrt{3}$  monolayer, the change in  $q_{st}$  with temperature and coverage is consistent with the evolution of a region in the phase diagram where two surface phases are in equilibrium. The same region can also be traced out from the manner in which the calorimeter system approaches equilibrium after the addition of an increment of gas. The results suggest that the apparent critical temperature for the two-phase region is at least 120 K, which is somewhat higher than estimates made from other types of experiments. In the multilayer region,  $q_{st}$  shows variations with surface coverage of an expected kind and magnitude but with a remarkable exception. Beginning at a surface coverage of 1.7 layers at  $T=98$  K and at higher surface coverages at  $T=105$ , 108, and 112 K,  $q_{st}$  abruptly decreases by about two-thirds. The effect is interpreted as marking a region where a solid surface phase melts. To assist the parametrization of an ethylene-graphite interaction potential, a value is obtained for the heat of adsorption at zero coverage,  $q_{st}(0)=20.4 \pm 0.2$  kJ mol<sup>-1</sup>, at  $T=120$  K. At this temperature, the effects of surface heterogeneity and of clustering of the adsorbed molecules are clearly delineated and thus permit an extrapolation to be made with reasonable certainty.

### I. INTRODUCTION

During the past several years, a great deal of information has been obtained about the adsorption of ethylene on graphite. Measurements of adsorption isotherms<sup>1</sup> showed that, below the triple point of bulk ethylene (104.5 K), only a limited number of adsorbed layers is formed. Any additional gas added to the system formed bulk solid. This general observation was verified by neutron and x-ray diffraction measurements on the system.<sup>2-4</sup> The dynamics of motion of ethylene molecules on the graphite surface has also been studied both experimentally<sup>5</sup> and theoretically.<sup>6</sup> A summary of the deductions about the ethylene on graphite system is contained in a phase diagram proposed by Mochrie *et al.*<sup>4</sup> (see Fig. 3 of their paper). Recently, some additional information about the phase diagram has been obtained from measurements of heat capacities for submonolayer and monolayer coverages.<sup>7</sup>

In the experiments to be described in this paper, heats of adsorption of ethylene on graphite have been measured calorimetrically in the temperature region  $98 < T < 120$  K up to a surface coverage of 3.7 layers. The coverage dependence of the isosteric heat of adsorption displays some features which have been observed for the methane on graphite system<sup>8</sup> and which may be associated with general characteristics of a physisorbed system. There are, however, some specific features which pertain to the phase diagram of ethylene on graphite. Also, as was found for the methane on graphite study,<sup>8</sup> the manner in which the calorimeter approaches equilibrium can be used to indicate the boundaries of certain phase fields.

For the limited range of overlap, the view of the phase diagram of ethylene on graphite obtained from the

calorimetric measurements is similar to that constructed from the diffraction studies<sup>4</sup> but there are significant differences. For example, the calorimetry suggests that the two-phase region identified as submonolayer liquid + two-dimensional gas extends to rather higher temperatures ( $\geq 120$  K) than has been supposed. Moreover, the region where low apparent heats of adsorption are observed does not seem to correspond to a single region deduced on the basis of structural measurements.

### II. MEASUREMENTS

The adiabatic calorimeter and the technique of measuring heats of adsorption with it have been fully described elsewhere.<sup>9</sup> Briefly, the measurements are performed in a region of  $\pm 0.5$  K from a chosen mean temperature to which all of the results are corrected. Normally, heats of adsorption are measured but heats of desorption can also be measured provided that the vapor pressure of the adsorbed film is large enough—say greater than 10 Torr.

Ethylene of research purity (minimum 99.99%) was obtained from Matheson Gas and was used without further purification. The adsorbent (11.45 g) was Grafoil MAT (Union Carbide Corp.) of bulk density  $\sim 0.3$  g cm<sup>-3</sup> and specific surface  $\sim 24$  m<sup>2</sup> g<sup>-1</sup>. For later reference, the amount of ethylene adsorbed to form a  $\sqrt{3} \times \sqrt{3}$  monolayer is estimated to be  $2.7 \times 10^{-3}$  mol. This is the measure of surface coverage commonly used to normalize results of different sets of experiments.<sup>4,7</sup> Immediately prior to the present measurements, the calorimeter had been used for the study of the methane on Grafoil MAT system.<sup>8</sup> The only treatment given to the adsorbent between the two series of measurements was to evacuate it thoroughly at room temperature over several days.

### III. HEATS OF ADSORPTION

In the calorimetric experiments, the quantity actually measured is a change in the integral heat of adsorption  $\Delta Q$ .<sup>8</sup> We will only be concerned with the isosteric heat of adsorption  $q_{st}$  which is defined by

$$q_{st} = \Delta Q / \Delta n_a, \quad (1)$$

where  $\Delta n_a$  is the number of moles of gas adsorbed in a single increment.

The results of the measurements at mean temperatures of 98, 105, 108, 112, and 120 K are summarized in Figs. 1 and 2, where  $q_{st}$  is plotted against the amount adsorbed. Duplicate series of measurements were made at  $T = 120$  K for  $0 < n_a < 4.4 \times 10^{-3}$  mol. The results of the two series agree to well within 1% over the range of surface concentration covered. At some points at other temperatures, the equilibrium times after additions of gas were an hour or more and this effect reduced the probable accuracy of  $q_{st}$  appreciably. An indication of the estimated accuracies is given by the vertical bars attached to several specific plotted points.

The general form of  $q_{st}$  versus  $n_a$  displayed in Fig. 1 is well understood. After an initial sharp drop caused by energetic heterogeneity of the substrate surface,  $q_{st}$  increases on account of interactions between the adsorbed molecules. For  $n_a > 1.9 \times 10^{-3}$  mol,  $q_{st}$  falls abruptly as adsorption of the first layer is completed. The curves which are drawn to guide the eye show that  $q_{st}$  is temperature dependent here. This is also true for the region  $0.1 < n_a < 1/2 \times 10^{-3}$  mol where the form of the change of  $q_{st}$  with temperature suggests that it is caused by an increase in clustering of the adsorbed molecules as the temperature is decreased.

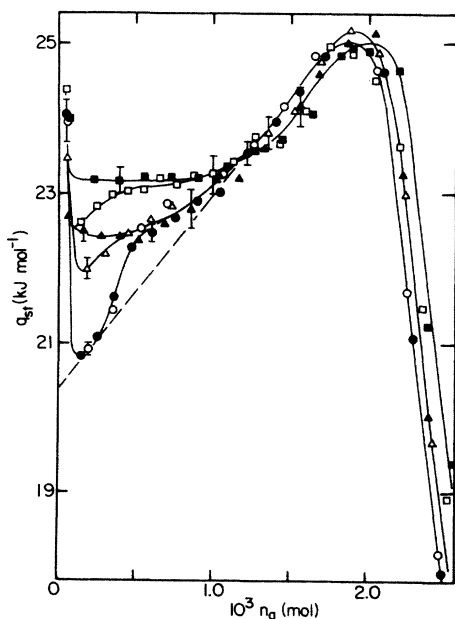


FIG. 1. Isosteric heat of adsorption of ethylene on graphite as a function of the amount adsorbed for the region less than a monolayer.  $\circ$ ,  $\bullet$ , 120 K;  $\triangle$ , 112 K;  $\blacktriangle$ , 108 K;  $\square$ , 105 K;  $\blacksquare$ , 98 K.

At the highest temperature,  $T = 120$  K, the apparent clustering only begins for  $n_a > 0.3 \times 10^{-3}$  mol. Thus, it is possible to perform an extrapolation, as indicated by the dashed curve in Fig. 1, to obtain an estimate of  $q_{st}$  for a single molecule of ethylene adsorbed on a uniform graphite surface. The result is  $q_{st}(0) = 20.4 \pm 0.2$  kJ mol<sup>-1</sup>, which is to be compared with 18.4 kJ mol<sup>-1</sup> obtained from chromatographic measurements<sup>10</sup> in the region  $313 < T < 403$  K, and 16.7 kJ mol<sup>-1</sup> for adsorption on graphitized carbon black at zero coverage and  $T = 183$  K.<sup>11</sup>

An estimate of the degree of energetic heterogeneity of the graphite surface can also be made from the data in Fig. 1. The excess heat of adsorption at the lowest surface coverages persists to a coverage of about 4.5% of a monolayer. The comparable result for methane adsorption on the same graphite specimen<sup>8</sup> is about 8%, which seems not unreasonable since methane is a smaller molecule.

The measured heats of adsorption for the multilayer region, which are displayed in Fig. 2, show a remarkable feature: except at  $T = 120$  K, the value of  $q_{st}$  suddenly drops to about 5 kJ mol<sup>-1</sup> and then remains at that level. An interpretation of this result will be proposed in Sec. V in connection with a discussion of the phase diagram for ethylene on graphite.

Figure 3 illustrates a different aspect of the adsorption. In the study of the CH<sub>4</sub> on graphite system, it was found<sup>8,12</sup> that extensive adsorption hysteresis occurred in the multilayer region. One way in which this was manifested was through systematic shifts of  $q_{st}$  with surface concentration after desorption from higher surface coverages. The system of ethylene on graphite was tested to a limited extent for hysteresis, and the results are given in Fig. 3. When the desorption was carried out at the same temperature as the adsorption,  $q_{st}$  was shifted systematically as observed previously.<sup>8,12</sup> In one experiment, adsorption at  $T = 120$  K was followed by desorption at  $T = 140$  K (where the vapor pressure was higher) and then  $q_{st}$  was again measured at  $T = 120$  K. It is evident from Fig. 3 that this procedure altered the "profile" of  $q_{st}$

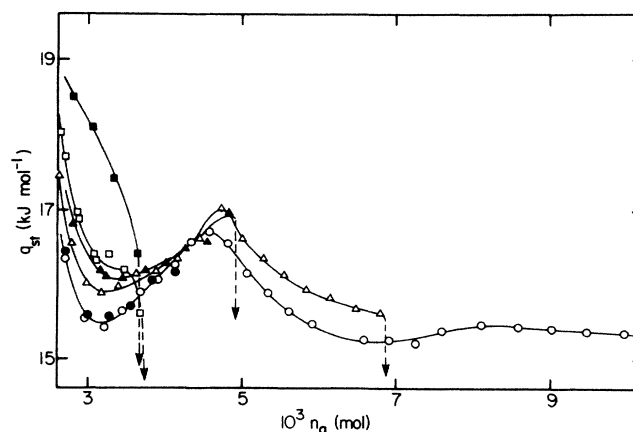


FIG. 2. Isosteric heat of adsorption of ethylene on graphite as a function of the amount adsorbed for the multilayer region. Symbols as in Fig. 1.

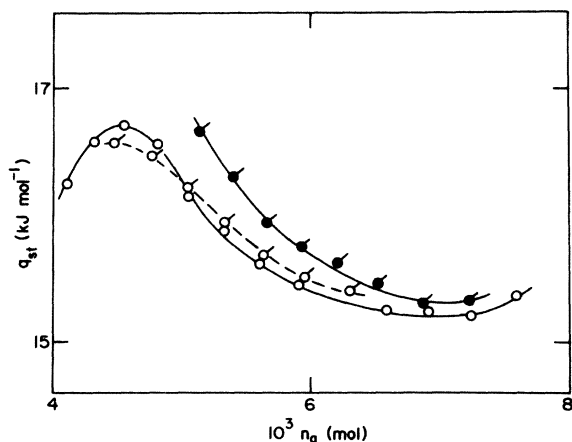


FIG. 3. Isosteric heat of adsorption of ethylene on graphite as a function of the amount adsorbed at  $T=120$  K.  $\circ$  as in Fig. 2.  $\oslash$ , after desorption from  $n_a=10.3 \times 10^{-3}$  mol at  $T=140$  K.  $\odot$ , after desorption from  $n_a=9.6 \times 10^{-3}$  mol at  $T=120$  K.

versus surface coverage. That fact may be significant for understanding the basis of the hysteresis but it was not pursued further for the ethylene on graphite system.

#### IV. THERMAL EQUILIBRATION

In all of the thermal measurements, the manner in which the temperature of the calorimeter vessel approached equilibrium after additions of gas was monitored closely. Either of two trends was observed. In one, the temperature of the vessel increased continuously and ultimately flattened off to a constant value. In the other, the temperature first rose and then fell by a moderate amount before flattening off. The temperature-time

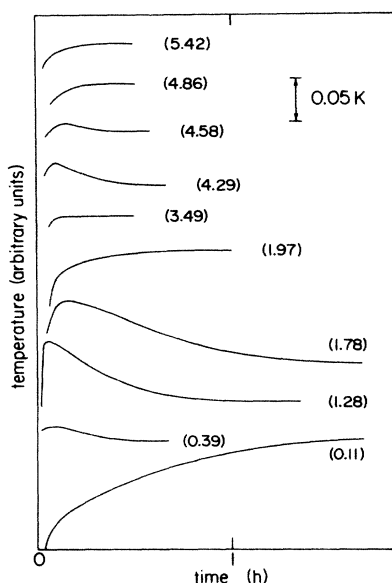


FIG. 4. Temperature of the calorimeter vessel as a function of time after additions of gas at amounts adsorbed indicated in parentheses (in units of  $10^{-3}$  mol).

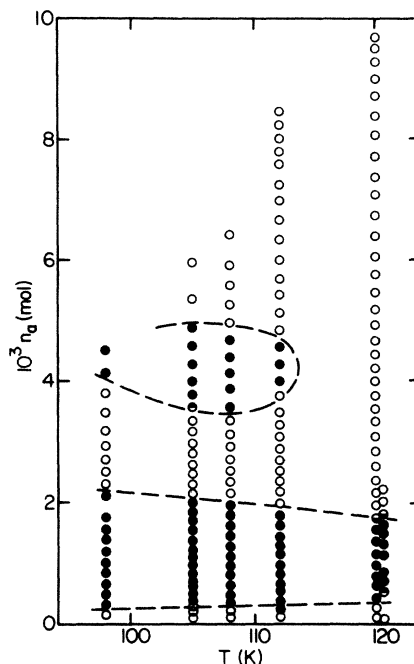


FIG. 5. Diagram depicting two types of temperature-time trends of the calorimeter vessel after additions of gas.  $\circ$ , continuous increase of temperature to an equilibrium value.  $\bullet$ , temperature increase followed by a decrease to an equilibrium value.

curves for one-quarter of the measurements at  $T=112$  K are illustrated in Fig. 4. The notable feature is the shift from one form of trend to the other as the surface coverage is changed. Similar general behavior was displayed at the other experimental temperatures. All of the results are brought together in Fig. 5 and two types of areas are delineated which we propose should be associated with one-phase (open circles) and two-phase (solid circles) regions. The simple argument for this proposition is the following.

The calorimeter system is operated adiabatically. Thus, if an increment of gas is adsorbed into a single surface phase, the temperature of the calorimeter vessel would be expected to rise smoothly to an equilibrium value. If, however, adsorption were to be followed by redistribution of the adsorbate between two surface phases, e.g., from condensed to expanded, a different temperature-time profile would result: an increase of temperature followed by a decrease to an equilibrium value.

Some support for the proposition is provided by the  $q_{st}$  data shown in Fig. 1. For the range  $0.2 \times 10^{-3} < n_a < 2.0 \times 10^{-3}$  mol at all of the temperatures studied, the heats of adsorption are characteristic of adsorption in a two-phase region.

#### V. CORRELATION WITH OTHER PHASE INFORMATION

The elements of the phase diagram outlined by the dashed curves in Fig. 5 are superimposed in Fig. 6 on

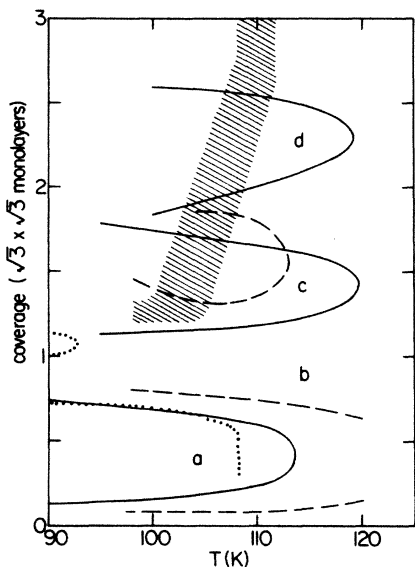


FIG. 6. A portion of the phase diagram for ethylene on graphite: — Mochrie *et al.* (Ref. 4). ···· Kim *et al.* (Ref. 7). --- present calorimetric measurements. Cross-hatching represents region of low  $q_{st}$ . Identification of regions from Ref. 4: a—submonolayer liquid + two-dimensional gas; b—monolayer liquid; c—monolayer liquid + fluid bilayer; d—fluid bilayer + prewetting film.

features gleaned from structural<sup>4</sup> and heat-capacity<sup>7</sup> measurements. The designation of the different regions is given in the caption for the figure. There is a general correspondence with respect to the two-phase region marked *a*, although, obviously, the different types of measurements give moderately different estimates of the liquid-gas critical temperature. It is possible that fluctuations in the two-dimensional system affect the different kinds of experiments in different ways but thermal equilibrium may also be significant. As the results in Fig. 4 show, the equilibrium times for the calorimeter system varied widely with surface coverage. At temperatures below 112 K, the equilibrium times became longer in general and, in some cases, were a few hours.

The lightly shaded area in Fig. 6 depicts the region over which very low values of  $q_{st}$ —of the magnitude of 5 kJ mol<sup>-1</sup>—were observed. It is very unlikely that the apparent dramatic decrease in  $q_{st}$  was caused by a part of each gas increment being trapped in the filling tube outside of the calorimeter vessel. In the first place, the pressure in the system was monitored continuously and found not to be affected by changes in the temperature of the filling tube. In the second place, the lower heats of adsorption were observed both above and below the melting temperature of bulk ethylene (104.5 K). Bulk solid caught in a narrow tube can only be removed slowly by sublimation but bulk liquid moves easily under a very small pressure gradient.

If a large portion of each gas increment were to be condensed as bulk solid or liquid on the wall of the calorimeter vessel rather than on the graphite surface, the effect on

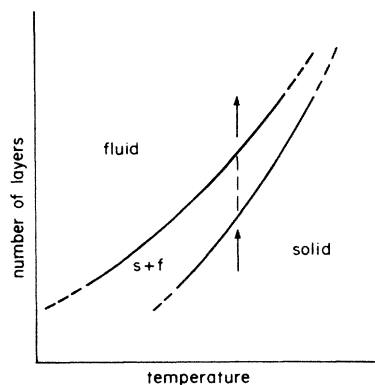


FIG. 7. Hypothetical surface-fluid—surface-solid coexistence region. The arrows indicate an isothermal adsorption path.

the apparent heat of adsorption would be small. For instance, the heat of vaporization of ethylene at  $T = 112$  K can be computed from the calorimetric data of Egan and Kemp<sup>13</sup> and is found to be 15.5 kJ mol<sup>-1</sup>. As Fig. 2 shows, in the multilayer region up to the equivalent of 2.6 layers adsorbed,  $q_{st}$  at  $T = 112$  K varies between 15.8 and 17 kJ mol<sup>-1</sup>.

We believe it is much more probable that the sudden decrease in  $q_{st}$  is caused by the melting of a solid bilayer or trilayer of the adsorbed ethylene. Without detailed structural information on the adsorbed phase, we cannot develop a quantitative explanation of the results at this time.

To account for the sharp decrease in the apparent  $q_{st}$ , a process is needed which "consumes" some of the energy which is released in the calorimeter vessel as the result of the adsorption of an increment of gas. A melting process has that characteristic but a little arithmetic shows that melting of an amount equivalent to each increment does not represent a large enough consumption of energy. The heat of fusion of an adsorbed layer is unlikely to be greater than the heat of fusion of bulk ethylene which is<sup>13</sup> 3.4 kJ mol<sup>-1</sup>. Thus, the melting of a complete increment might be expected to reduce the apparent  $q_{st}$  from 16 kJ mol<sup>-1</sup> to not less than 12.6 kJ mol<sup>-1</sup> and certainly not to  $\sim 5$  kJ mol<sup>-1</sup>.

This, however, is an oversimplified view. The effect of melting could easily be amplified as we shall show using the diagram in Fig. 7. It depicts a hypothetical surface-fluid—surface-solid coexistence region of a phase diagram. The isothermal path along which the heats of adsorption are measured is indicated by the arrows. In the two-phase region, after the addition of an increment of gas, the ratio of fluid to solid is changed by an amount which depends on the slopes of the phase boundary curves. That amount could be large if the slopes are shallow.

In principle, very extensive measurements of heats of adsorption could refine the region of the phase diagram indicated by the shaded area in Fig. 6. Before those are undertaken, however, it is essential to have the guidance of more structural information about the bilayer and the trilayer. A bilayer identified by Mochrie *et al.*<sup>4</sup> appears to have a melting temperature below 98 K.

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